Highly efficient fullerene and non-fullerene based ternary organic solar cells incorporating a new tetrathiocin-cored semiconductor

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Synthetic procedures of all new compounds presented in the main manuscript

General

For all reactions carried out in anhydrous conditions, glassware was dried in an oven at 130°C. Reagents were purchased from commercial sources without further purification unless otherwise stated. Dry solvents were obtained from a solvent purification system (SPS 400 by Innovative Technologies) with an alumina drying agent. 1H and 13C NMR spectra were recorded on DRX 500 or AV3 400 at 500 and 125 MHz or 400 and 100 MHz, respectively. Chemical shifts are in ppm and J values are in Hz. Low resolution mass spectrometry (LRMS) was performed on a Shimadzu Axima-CFR spectrometer (MALDI). Elemental analyses were performed on a Perkin-Elmer 2400 analyser. Melting points were determined using a Stuart Scientific SMP1 Melting Point apparatus and are uncorrected.
Synthetic procedure for the synthesis of compound 1 in the main manuscript – EH-5T-HU

EH-5T-HU was prepared from 3-bromothiophene (1) by first appending the 2-ethylhexyl group via a Kumada coupling to give 2. The 5-position of the thiophene ring was then capped with a methyl group utilising LiTMP to selectively lithiate the less hindered position, and trapping with methyl iodide to give 3. After bromination with N-bromosuccinimide, 4 was coupled to tributyl(thiophen-2-yl)stannane giving the bithiophene system 5, which was then formylated using DMF as a formyl cation equivalent. Vinylene trithiocarbonate (7) was then sequentially lithiated with LDA followed by addition of 6 to generate an intermediate diol that was quickly oxidised with MnO₂ to give 8. The 1,3-dithiole-2-thione system was then transchalcogenated using Hg(OAc)₂ to give the carbonyl derivative, which underwent a Paal-Knorr thiophene synthesis with phosphorus pentasulfide to give EH-5T-HU.

Scheme 1: Synthesis of EH-5T-HU. Reagents and conditions: i) C₈H₁₇MgBr, Ni(dpdp)Cl₂, THF, reflux ii) LiTMP, THF, -80°C, then MeI iii) N-bromosuccinimide, CHCl₃/AcOH, r.t. iv) tributyl(thiophen-2-yl)stannane, Pd(PPh₃)₄, DMF, 150°C v) n-BuLi, THF, -80°C, then DMF vi) LDA, THF, -60°C vii) MnO₂, CH₂Cl₂ viii) Hg(OAc)₂, CH₂Cl₂/AcOH ix) P₂S₅ NaHCO₃, 1,4-dioxane.
**Experimental**

All reactions were performed under an inert atmosphere of nitrogen.

2-Ethylhexyl bromide (20.45 ml, 115 mmol) was added to magnesium turnings (2.91 g, 120 mmol) in anhydrous THF (15 ml), refluxed for 1 hr and then added drop-wise via cannula to a solution of 3-bromothiophene (8.91 ml, 92 mmol) and Ni(dppp)Cl$_2$ (0.25 g, 0.46 mmol) in anhydrous THF (50 ml). The reaction mixture was left to stir overnight, quenched with 2N HCl (30 ml) and extracted into diethyl ether (3 × 50 ml). The combined organic extracts were dried over anhydrous magnesium sulfate, concentrated under reduced pressure then purified via kugelrohr distillation (8 mbar, 115 - 120°C) followed by column chromatography (silica, hexane) to give 3-(2-ethylhexyl)thiophene (9.04 g, 50%) as a colourless oil. $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 7.23 (1H, m, ThH), 6.91 (2H, m, ThH), 2.57 (2H, d, $J = 7.0$ Hz, ThCH$_2$), 1.56 (1H, m, CH), 1.28 (8H, m, CH$_2$), 0.89 (6H, m, CH$_3$); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 148.1, 129.0, 124.9, 120.8, 40.6, 34.5, 332.7, 29.1, 25.8, 23.2, 14.3, 11.0.

$n$-Butyllithium (28.2 ml, 2.35 M in hexanes, 67.8 mmol) was added drop-wise to a solution of tetramethylpiperidine (12.0 ml, 70.5 mmol) in anhydrous THF (50 ml) at -80°C and left to stir for 1 hr. The solution was then added slowly via cannula to a solution of 3-(2-ethylhexyl)thiophene (11.51 g, 58.9 mmol) in anhydrous THF (50 ml) at -80°C and left to stir for a further 1 hr. Iodomethane (7.34 ml, 117.8 mmol) was added and the solution left to stir overnight at room temperature, then quenched with
water (50 ml) and extracted into diethyl ether (3 × 50 ml). The combined organic extracts were washed with water (30 ml), saturated NaHCO₃ solution (30 ml), water (30 ml), 2N HCl (30 ml) and brine (30 ml) then dried over anhydrous magnesium sulfate and concentrated under reduced pressure. The crude material was then run through a silica plug eluting with hexane and concentrated under reduced pressure to give 4-(2-ethylhexyl)-2-methylthiophene (10.8 g, 87%) as a colourless oil. ¹H NMR (400 MHz, CDCl₃) δ 6.67 (1H, m, ThH), 6.61 (1H, m, ThH), 2.51 (2H, d, J = 7.2 Hz, ThCH₂), 2.50 (3H, d, J = 0.8 Hz, ThCH₃), 1.57 (1H, m, CH), 1.33 (8H, m, CH₂), 0.93 (6H, m, CH₃); ¹³C NMR (100 MHz, CDCl₃) δ = 141.9, 139.1, 127.3, 118.3, 40.4, 34.7, 32.7, 29.1, 25.7, 23.2, 15.5, 14.3, 11.0. LRMS (EI, m/z) calc. for C₁₃H₂₂S: 210 (M⁺), found 211 (M + H)⁺.

\[
\begin{align*}
\text{C}_2\text{H}_5 & \quad \text{C}_4\text{H}_9 \\
\text{S} & \quad \text{Br}
\end{align*}
\]

Under exclusion of light, N-bromosuccinimide (9.09 g, 51.1 mmol) was added to a solution of 5-methyl-3-(2-ethylhexyl)thiophene (10.74 g, 51.1 mmol) in chloroform (75 ml) and acetic acid (75 ml) and left to stir overnight. The resultant solution was then washed with water (3 × 50 ml) and neutralised with saturated NaHCO₃ solution before being dried over anhydrous magnesium sulfate and concentrated under reduced pressure. The crude product was then purified via kugelrohr distillation (6.67 mbar, 150 - 155°C) followed by a silica plug eluting with hexane to give 2-bromo-3-(2-ethylhexyl)-5-methylthiophene (10.1 g, 70%) as a pale yellow oil. ¹H NMR (400 MHz, CDCl₃) δ 6.43 (1H, m, ThH), 2.41 (2H, d, J = 7.2 Hz, ThCH₂), 2.39 (3H, s, ThCH₃), 1.56 (1H, m, CH), 1.28 (8H, m, CH₂), 0.88 (6H, m, CH₃). ¹³C NMR (100 MHz, CDCl₃) δ 141.2, 139.2, 127.1, 105.9, 40.1, 33.9, 33.9, 32.6, 29.0, 25.8, 23.2, 14.3, 11.0. LRMS (EI, m/z) calc. for C₁₃H₂₁SBr: 289 (M⁺), found 289 (M⁺).

\[
\begin{align*}
\text{C}_2\text{H}_5 & \quad \text{C}_4\text{H}_9 \\
\text{S} & \quad \text{S}
\end{align*}
\]
Tetrakis(triphenylphosphine)palladium (1.46 g, 0.50 mmol) was added to a degassed solution of 2-bromo-3-(2-ethylhexyl)-5-methylthiophene (7.30 g, 25.24 mmol) and 2-(tributylstannyl)thiophene (10.0 ml, 31.55 mmol) in anhydrous DMF (100 ml) and refluxed overnight. After cooling to room temperature, the solution was filtered through Celite washing through with diethyl ether. The filtrate was then treated with aqueous potassium fluoride solution (1 M, 130 ml), re-filtered through Celite, washed with saturated NH₄Cl solution (50 ml), dried over anhydrous magnesium sulfate and concentrated under reduced pressure. The crude product was then purified via column chromatography (silica, hexane) to give 3-(2-ethylhexyl)-5-methyl-2,2'-bithiophene (4.40 g, 62%) as a colourless oil. 

\[
{^1}H\text{ NMR (400 MHz, CDCl}_3\) \delta 7.25 (1H, m, ThH), 7.03 (2H, m, ThH), 6.56 (1H, m, ThH), 2.60 (2H, d, J = 7.6 Hz, ThCH₂), 2.44 (3H, d, J = 1.2 Hz, ThCH₂), 1.59 (1H, m, CH), 1.26 (8H, m, C₆H₃), 0.83 (6H, m, C₆H₃); \]

\[
{^{13}}C\text{ NMR (100 MHz, CDCl}_3\) \delta 139.1, 138.0, 136.8, 128.9, 128.7, 127.3, 125.9, 125.0, 40.4, 33.5, 32.7, 28.8, 25.9, 23.2, 15.4, 14.3, 10.9. LRMS (EI, m/z) calc. for C₁₇H₂₄S₂: 293 (M⁺), found 293 (M⁺).
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\[
\text{C}_2\text{H}_9\text{C}_4\text{H}_9\text{S} = \text{O}
\]

\[n\text{-Butyllithium (7.50 ml, 2.35 M in hexanes, 17.6 mmol) was added drop-wise to a solution of 3-(2-ethylhexyl)-5-methyl-2,2'-bithiophene (4.63 g, 15.8 mmol) in anhydrous THF (60 ml) at -80°C. After stirring at -80°C for 2 hrs, anhydrous DMF (2.45 ml, 31.6 mmol) was added, the resultant solution stirred at -80 °C for 1 hr, then left acquire room temperature and stir overnight. The reaction was then poured into water (200 ml), extracted into ethyl acetate (3 × 80 ml), washed with brine (50 ml), dried over anhydrous magnesium sulfate and concentrated under reduced pressure. The crude product was then purified via column chromatography (silica, 1:1 hexane:chloroform) to give 3'- (2-ethylhexyl)-5'-methyl-[2,2'-bithiophene]-5-carbaldehyde (4.89 g, 96%), as an orange oil. {^1}H\text{ NMR (400 MHz, CDCl}_3\) \delta 9.86 (1H, s, CHO), 7.67 (1H, d, J = 4.0 Hz, ThH), 7.10 (1H, d, J = 4.0 Hz, ThH), 6.61 (1H, m, ThH),
\]
2.67 (2H, d, \( J = 7.2 \) Hz, Th\( \text{CH}_2 \)), 2.46 (3H, d, \( J = 1.2 \) Hz, Th\( \text{CH}_3 \)), 1.63 (1H, m, CH), 1.28 (8H, m, \( \text{CH}_2 \)), 0.84 (6H, m, \( \text{CH}_3 \)); \(^{13}\text{C} \) NMR (100 MHz, CDCl\(_3\)) \( \delta \) 182.8, 147.4, 141.9, 141.7, 140.5, 137.0, 129.8, 127.9, 126.0, 40.3, 34.0, 32.6, 28.8, 25.9, 23.2, 15.5, 14.3, 10.9; LRMS (MALDI, \( m/z \)) calc. for C\(_{18}\)H\(_{24}\)OS\(_2\): 321 (M\(^+\)), found 320 (M – H\(^+\)).

Lithium diisopropylamide solution (3.00 ml, 1.90 M in THF/heptanes/ethyl benzene, 5.60 mmol) was added drop-wise to a solution of 1,3-dithiole-2-thione (0.76 g, 5.60 mmol) in anhydrous THF (60 ml) at -60°C and left to stir for 20 min before a solution of 3’-(2-ethylhexyl)-5’-methyl-[2,2’-bithiophene]-5-carbaldehyde in anhydrous THF (40.0 ml, 0.14 mM, 5.60 mmol) was added and left to stir for a further 20 min at -60°C. A second equivalent of lithium diisopropylamide solution (3.00 ml, 1.90 M, 5.60 mmol) was added drop-wise, left to stir for 20 min then the solution was cooled to -80°C whereupon a second equivalent of 3’-(2-ethylhexyl)-5’-methyl-[2,2’-bithiophene]-5-carbaldehyde solution (anhydrous THF) (40.0 ml 0.14 mM, 5.60 mmol) was added. After stirring for a further 20 min at -60°C, the solution was allowed to warm to room temperature, before being poured into saturated NaHCO\(_3\) solution (280 ml) to which potassium bromide (28 g) was added. The mixture was extracted into ethyl acetate (3 \( \times \) 200 ml) and the combined organic extracts dried over anhydrous magnesium sulfate and concentrated under reduced pressure to give a dark oil. The crude material (6.00 g) was immediately dissolved in dichloromethane (120 ml) to which manganese (IV) oxide (10 fold w/w excess, 60 g) was added, stirred at room temperature for 1 min and then run through a silica plug eluting with dichloromethane. All product containing washings were combined, concentrated under reduced pressure and then purified via column chromatography (silica, 5:2 hexane:CH\(_2\)Cl\(_2\)) to give (2-thioxo-1,3-dithiole-4,5-diyl)bis((3’-(2-ethylhexyl)-5’-methyl-[2,2’-bithiophen]-5-yl)methanone) (2.99 g, 51%) as a viscous deep red oil. \(^1\text{H} \) NMR (400 MHz, CDCl\(_3\)) \( \delta \) 7.61 (2H, d, \( J = 4.0 \) Hz, Th\( \text{H} \)), 7.03 (2H, d, \( J \)
= 4.0 Hz, ThH), 6.58 (2H, m, ThH), 2.58 (4H, d, J = 7.2 Hz, ThCH2), 2.43 (6H, d, J = 0.8 Hz, ThCH3),
1.57 (2H, m, CH), 1.23 (16H, m, CH2), 0.82 (12H, m, CH3); 13C NMR (100 MHz, CDCl3) δ 208.0,
175.3, 150.0, 144.4, 142.4, 141.3, 139.9, 136.2, 130.0, 127.8, 126.0, 40.2, 34.2, 32.7, 28.8, 25.9, 23.1,
15.5, 14.1, 10.8. LRMS (MALDI, m/z) calc. for C39H46O3S7: 771 (M+), found 772 (M + H)+.

Mercury (II) acetate (1.73 g, 5.40 mmol) was added to a solution of (2-thioxo-1,3-dithiole-4,5-diyl)
bis((3’-(2-ethylhexyl)-5’-methyl-[2,2'-bithiophen]-5-yl)methanone) (2.99 g, 3.90 mmol) in
dichloromethane (120 ml) and acetic acid (40 ml) and left to stir for 24 hrs at room temperature. The
resultant suspension was run through a silica plug eluting with dichloromethane, washed with water (3
× 200 ml), neutralised with saturated NaHCO3 solution (200 ml), dried over anhydrous magnesium
sulfate and concentrated under reduce pressure to give (2-oxo-1,3-dithiole-4,5-diyl)bis((3’-(2-
ethylhexyl)-5’-methyl-[2,2'-bithiophen]-5-yl)methanone) (2.84 g, 97%) as a viscous deep red oil. 1H
NMR (400 MHz, CDCl3) δ 7.58 (2H, d, J = 4.0 Hz, ThH), 7.02 (2H, d, J = 4.4 Hz, ThH), 6.57 (2H, m,
ThH), 2.57 (4H, d, J = 7.2 Hz, ThCH2), 2.43 (6H, d, J = 0.4 Hz, ThCH3), 1.57 (2H, m, CH), 1.23 (16H,
m, CH2), 0.82 (12H, m, CH3); 13C NMR (100 MHz, CDCl3) δ 187.4, 466.5, 149.6, 142.2, 141.1, 140.2,
136.0, 135.5, 129.9, 127.8, 125.9, 40.2, 34.2, 32.7, 28.8, 25.8, 23.1, 15.5, 14.1, 10.8. LRMS (MALDI,
m/z) calc. for C39H46O3S6: 755 (M+), found 754 (M - H)+.

A mixture of (2-oxo-1,3-dithiole-4,5-diyl)bis((3’-(2-ethylhexyl)-5’-methyl-[2,2'-bithiophen]-5-
yl)methanone) (2.84 g, 3.80 mmol), sodium hydrogen carbonate (1.58 g, 18.8 mmol) and phosphorus
pentasulfide (8.36 g, 18.8 mmol) in anhydrous 1,4-dioxane (100 ml) was heated to 60°C then the
temperature was gradually increased to 90°C over the course of 30 min. The reaction was then left to
stir for 3 hrs at 90°C before cooling to room temperature. Water (100 ml) was slowly added and the
resulting suspension refluxed for 1 hr then left to stir at room temperature overnight before being filtered
and washed with water (300 ml) and cold methanol (200 ml). The crude solid was collected, dissolved
in the minimum amount of hot ethanol and allowed to cool overnight. The resultant precipitate was
filtered, washed with cold methanol and dried overnight in a desiccator to give 4,6-bis(3'-(2-
ethylhexyl)-5'-methyl-[2,2'-bithiophen]-5-yl)thieno[3,4-d][1,3]dithiol-2-one (2.40 g, 87%) as an
orange/red solid (mp 99 – 101°C). \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.12 (2H, d, \(J = 4.0\) Hz, ThH), 7.00
(2H, d, \(J = 3.6\) Hz, ThH), 6.56 (2H, s, ThH), 2.62 (4H, d, \(J = 7.2\) Hz, ThCH\(_2\)), 2.44 (6H, s, ThCH\(_3\)),
1.61 (2H, m, CH), 1.28 (16H, m, CH\(_2\)), 0.84 (12H, m, CH\(_3\)). \(^1\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 139.9,
139.0, 138.1, 133.6, 129.5, 127.9, 126.5, 125.7, 125.5, 124.2, 40.5, 33.8, 32.8, 29.0, 25.9, 23.3, 15.6,
14.4, 11.0; LRMS (MALDI, \(m/z\)) calc. for C\(_{39}\)H\(_{46}\)O\(_2\)S\(_7\): 755 (M\(^+\)), found 754 (M – H)^+.

Freshly prepared sodium methoxide solution (0.744 M in anhydrous methanol, 0.61 ml, 0.453 mmol)
was added drop-wise to a solution of 4,6-bis(3'-(2-ethylhexyl)-5'-methyl-[2,2'-bithiophen]-5-
yl)thieno[3,4-d][1,3]dithiol-2-one (0.114 g, 0.151 mmol) in anhydrous THF (20 ml) at room
temperature under nitrogen. After refluxing for 15 mins, the dark solution was cooled to room
temperature before iodine solution (0.0965 M in anhydrous THF, 1.88 ml, 0.181 mmol) was added
drop-wise to give a red/orange solution. After stirring at room temperature for 1 hr, the reaction was quenched with aqueous sodium thiosulfate solution (10 ml), poured into water (100 ml) and extracted into CH$_2$Cl$_2$ (3 × 50 ml). The combined organic extracts were washed with water, dried over anhydrous magnesium sulfate and concentrated under reduced pressure. The resulting crude red solid was dissolved in CH$_2$Cl$_2$ and run through a short silica plug eluting with CH$_2$Cl$_2$. All coloured material was collected and combined then concentrated to approximately 5 ml and precipitated with methanol (100 ml) to give an orange precipitate, which was collected via filtration and dried under vacuum to give EH-5T-TTC (0.070 g, 64 %) as a red solid (mp 142 - 144°C).

$^1$H NMR (600 MHz, CDCl$_3$) δ 7.41 (4H, d, $J = 3.8$ Hz, ThH), 7.03 (4H, d, $J = 3.8$ Hz, ThH), 6.59 (4H, s, ThH), 2.69 (8H, dd, $J = 7.1, 1.9$ Hz, CH$_2$), 2.47 (12H, s, ThCH$_3$), 1.64 (4H, m, CH), 1.34 – 1.23 (32H, br m, CH$_2$), 0.83 (24H, m, CH$_3$); $^{13}$C NMR (125 MHz, CDCl$_3$) δ 141.0, 139.9, 139.8, 138.7, 133.6, 132.5, 129.4, 128.4, 128.2, 125.6, 40.4, 33.9, 32.7, 28.8, 25.9, 23.2, 15.5, 14.3, 10.9; LRMS (MALDI, m/z) calc. for C$_{76}$H$_{92}$S$_{14}$ (M$^+$): 1452.33, found 1453.06; Elemental analysis, calc: C 62.79, H 6.38, found: C 62.80, H 6.14. T$_d$ 318 °C.

Sodium methoxide solution (0.876 M in anhydrous methanol, 1.37 ml, 1.20 mmol) was added dropwise to a solution of 4,6-bis(3’-(2-ethylhexyl)-5’-methyl-[2,2’-bithiophen]-5-yl)thieno[3,4-d][1,3]dithiol-2-one (0.302 g, 0.400 mmol) in anhydrous THF (50 ml) at room temperature. After refluxing for 15 mins, the dark solution was cooled to room temperature and freshly prepared (under an inert atmosphere) germanium (IV) bromide solution (0.167 M in anhydrous THF, 1.32 ml, 0.220 mmol) added dropwise. The resultant orange solution was stirred for 45 mins at room temperature, then quenched with 2N HCl
(3 ml), poured into water (100 ml) and extracted into CH₂Cl₂ (3 × 75 ml). The combined organic extracts were washed with water (2 × 100 ml) dried over anhydrous magnesium sulfate and concentrated under reduced pressure to give an orange/red oil. The crude product was dissolved in CH₂Cl₂ and run through a short silica plug before concentrating to dryness. The residue was then dissolved in hot hexane (150 ml), filtered whilst hot and left to cool in the freezer overnight. The resultant precipitate was collected, washed with cold hexane (2 × 50 ml) and dried under high vacuum in a dessicator to give EH-5T-Ge (0.203 g, 66%) as an orange solid (mp 83 - 85 °C). ¹H NMR (400 MHz, CDCl₃) δ 7.30 (4H, d, J = 3.9 Hz, ArH), 7.00 (4H, d, J = 3.9 Hz, ArH), 6.57 (4H, s, ArH), 2.65 (8H, m, CH₂), 2.44 (12H, s, ArCH₃), 1.63 (4H, m, CH₂), 1.30 (32H, m, CH₂), 0.86 (24H, m, CH₃); ¹³C NMR (100 MHz, CDCl₃) δ 139.6, 138.6, 137.5, 134.6, 129.3, 128.8, 128.3, 126.1, 125.9, 40.5, 33.8, 32.8, 28.9, 25.8, 23.3, 15.3, 14.3, 10.9; LRMS (MALDI, m/z) calc. for C₇₆H₉₂GeS₁₄: 1526.25, found 1526.79 (M⁺); Elemental analysis, calc: C 59.78, H 6.07, found: C 59.94, H 5.87. Td 383 °C.

Single crystal X-ray diffraction

A suitable crystal for EH-5T-TTC was selected and data collected following a standard method⁴, on a Rigaku AFC12 goniometer at 100K equipped with an enhanced sensitivity (HG) Saturn724+ detector mounted at the window of an FR-E-Superbright molybdenum anode generator with VHF Varimax optics (70µm focus).

Cell determination and data collection were carried out using CrystalClearii, with data reduction, cell refinement and absorption correction carried out using CrysAlisProiii. Within Olex2iv, the structures were solved using SHELXTv and refinement using SHELXLvi.

Crystal data for EH-5T-TTC : C₇₆H₉₂S₁₄, M_r = 1454.33, red plate, monoclinic, P2₁/c, a = 16.8658(8) Å, b = 24.1932(7) Å, c = 9.1640(5) Å, β = 100.116(5)°, α = γ = 90°, V = 3681.1(3) Å³, T = 100(2) K, Z = 2, Z’ = 0.5, μ(MoKα) = 0.455 mm⁻¹, 52641 reflections measured, 8374 unique (R_int = 0.0725). R1 = 0.0688, wR2 = 0.1716 [F^2 > 2σ(F^2)], R1 = 0.1299, wR2 = 0.2043 (all data).
Supplementary Figures

Figure S1. (a) Energy level diagram of the binary blend components and the ternary components. (b) The spectral overlap between the UV-Vis absorption spectra of PTB7-Th and the photoluminescence spectra of the ternary donor components.
Figure S2. (a) Comparison of PCE and (b) J-V characteristics of the of binary PTB7-Th:ITIC and ternary blend systems.

Figure S3. UV-Vis absorption spectra of the PTB7-Th:ITIC as a function of different EH-5T-TTC content.

Table S1. Photovoltaic performance parameters of the binary PTB7-Th:EH-IDTBR and PTB7-Th:EH-IDTBR:EH-5T-TTC blend systems. $J_{sc}$ estimated from EQE spectra is also shown.
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<th>EH-5T-TTC (wt%)</th>
<th>Jsc/(EQE) (mA/cm²)</th>
<th>Voc (V)</th>
<th>FF (%)</th>
<th>Rsh (Ωcm²)</th>
<th>Rs (Ωcm²)</th>
<th>PCE (%) avg</th>
<th>PCE best (%)</th>
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<tr>
<td>0</td>
<td>12.81±0.27</td>
<td>1.02±0.01</td>
<td>56.7±0.5</td>
<td>594±68</td>
<td>1.66±0.35</td>
<td>7.46±0.17</td>
<td>7.82</td>
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<td>(13.5±0.4)</td>
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<tr>
<td>10</td>
<td>15.35±0.39</td>
<td>0.965±0.005</td>
<td>59.7±0.77</td>
<td>736±172</td>
<td>1.35±0.20</td>
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<tr>
<td>(15.5±0.5)</td>
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Figure S4. (a) Absorption spectra of the binary PTB7-Th:PC71BM and ternary PTB7-Th:PC71BM:EH-5T-TTC; (b) energy level diagram of the three components in the blend system: (c) J-V characteristics of the best ternary OPV devices; (d) the EQE spectra of the binary and ternary blend systems compared.
Table S2. Photovoltaic performance parameters of the binary PTB7-Th:PC$_{71}$BM and PTB7-Th:PC$_{71}$BM:EH-5T-TTC blend systems. $J_{sc}$ estimated from EQE spectra is also shown.

<table>
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<tr>
<th>DIO</th>
<th>EH-5T-TTC (wt%)</th>
<th>$J_{sc}$/(EQE) (mA/cm$^2$)</th>
<th>$V_{oc}$ (V)</th>
<th>FF (%)</th>
<th>$R_{sh}$ (Ωcm$^2$)</th>
<th>Rs (Ωcm$^2$)</th>
<th>PCE (%)</th>
<th>PCE best (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>No</td>
<td>0</td>
<td>11.4±0.3 (12.3±0.3)</td>
<td>0.770±0.009</td>
<td>36.5±0.4</td>
<td>137±4.5</td>
<td>2.4±0.5</td>
<td>3.2±0.1</td>
<td>3.36</td>
</tr>
<tr>
<td>No</td>
<td>10</td>
<td>15.0±0.2 (14.9±0.4)</td>
<td>0.778±0.004</td>
<td>52.0±0.6</td>
<td>370±33</td>
<td>2.0±0.2</td>
<td>6.09±0.24</td>
<td>6.31</td>
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<tr>
<td>Yes</td>
<td>0</td>
<td>16.3±0.95 (16.8±0.5)</td>
<td>0.772±0.003</td>
<td>71.9±0.6</td>
<td>1200±468</td>
<td>1.11±0.22</td>
<td>9.02±0.45</td>
<td>9.42</td>
</tr>
<tr>
<td>Yes</td>
<td>10</td>
<td>15.2±0.7 (16.4±0.5)</td>
<td>0.769±0.004</td>
<td>72.7±0.5</td>
<td>1480±553</td>
<td>1.12±0.26</td>
<td>8.50±0.35</td>
<td>8.82</td>
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</tbody>
</table>

Figure S5. (a) $J-V$ characteristics and the corresponding (b) EQE spectra of the PTB7-Th:PC$_{71}$BM and PTB7-Th:PC$_{71}$BM:EH-5T-TTC in the presence of DIO additive.
Figure S6. Variation of (a) \( J_{sc} \) and (b) \( V_{oc} \) as a function of light intensity for binary PTB7-Th:ITIC blend and EH-5T-TTC:PTB7-Th:ITIC ternary blend.

Figure S7. Atomic force microscopy images of the (a) PTB7-Th:ITIC and (b) PTB7-Th:ITIC:EH-5T-TTC blend films
<table>
<thead>
<tr>
<th></th>
<th>EH-5T-TTC</th>
<th>PTB7-Th</th>
<th>PC$_{71}$BM</th>
<th>ITIC</th>
<th>IDTBR</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>DI water</strong></td>
<td>![Image]</td>
<td>![Image]</td>
<td>![Image]</td>
<td>![Image]</td>
<td>![Image]</td>
</tr>
<tr>
<td><strong>Diododecane</strong></td>
<td>![Image]</td>
<td>![Image]</td>
<td>![Image]</td>
<td>![Image]</td>
<td>![Image]</td>
</tr>
<tr>
<td><strong>Ethylene glycol</strong></td>
<td>![Image]</td>
<td>![Image]</td>
<td>![Image]</td>
<td>![Image]</td>
<td>![Image]</td>
</tr>
</tbody>
</table>

**Figure S8.** Contact angle measurement of the each of the donor and acceptor components for three different solvents. These contact angle measurements have been used for the surface energy calculations.
Figure S9. Comparison of the exciton dissociation probability of binary and ternary blends of (a) PTB7:ITIC (b) PTB7-Th:EH-IDTBR and (c) PTB7-Th:PC$_{71}$BM with EH-5T-TTC.
Figure 10. Photoluminescence spectra of PTB7-Th and blends of PTB7-Th:EH-5T-TTC.
Figure S11: Photovoltaic performance parameters of the binary PTB7-Th:PC$_{71}$BM and ternary blend systems using EH-5T-HU and EH-5T-TTC.
Table S3. Photovoltaic performance parameters of the binary PTB7-Th:PC$_{71}$BM and ternary blend systems using EH-5T-HU and EH-5T-TTC. The average values of the device characteristics are given throughout, alongside their standard deviation, and the highest recorded PCE values are recorded in the final column. $J_{sc}$ estimated from EQE spectra is also shown.

<table>
<thead>
<tr>
<th>Blend</th>
<th>Jsc (mA/cm$^2$)</th>
<th>Voc (V)</th>
<th>FF (%)</th>
<th>Rs (Ohmcm$^2$)</th>
<th>Rsh (Ohmcm$^2$)</th>
<th>PCE (%)</th>
<th>PCE (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PTB7-Th:PC$_{71}$BM</td>
<td>10.6 ±0.48</td>
<td>0.770 ±0.005</td>
<td>37.9 ±0.34</td>
<td>2.64 ±0.51</td>
<td>136 ±4</td>
<td>3.1±0.14</td>
<td>3.33</td>
</tr>
<tr>
<td>PTB7-Th:PC$_{71}$BM.EH-5T-HU</td>
<td>12.2 ±0.4</td>
<td>0.756 ±0.013</td>
<td>43.5 ±0.71</td>
<td>2.41 ±0.61</td>
<td>183 ±13</td>
<td>4.02±0.20</td>
<td>4.26</td>
</tr>
<tr>
<td>PTB7-Th:PC$_{71}$BM.EH-5T-TTC</td>
<td>14.7 ±0.5</td>
<td>0.771 ±0.007</td>
<td>49.1 ±0.6</td>
<td>2.18 ±0.49</td>
<td>232.4 ±20.9</td>
<td>5.60±0.20</td>
<td>5.89</td>
</tr>
</tbody>
</table>
Figure S12. Shelf life of encapsulated ternary and binary solar cells under ambient conditions


Sheldrick, G.M., Acta Cryst., 2015, A71, 3-8

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